

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G03F 7/027</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/42549</b> <b>(43) International Publication Date:</b> 13 November 1997 (13.11.97)
<b>(21) International Application Number:</b> PCT/NL97/00261 <b>(22) International Filing Date:</b> 7 May 1997 (07.05.97)  <b>(30) Priority Data:</b> 60/017,211 9 May 1996 (09.05.96) US  <b>(71) Applicant:</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors:</b> LAPIN, Stephen, C.; 15 N. 082 Shirewood Farms Road, Hampshire, IL 60140 (US). SULLIVAN, Michael, G.; 512 S. Lake Street, Mundelein, IL 60060 (US).  <b>(74) Agent:</b> KRIJGSMAN, Willem; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTSENSITIVE RESIN.COMPOSITION FOR RAPID PROTOTYPING AND A PROCESS FOR THE MANUFACTURE OF 3-DIMENSIONAL OBJECTS  <b>(57) Abstract</b>  The invention relates to a photosensitive resin composition for rapid prototyping comprising: a) about 30 to about 70 wt.% of at least two epoxy resins, at least one of these resins is solid at room temperature, and comprises aromatic groups, and at least one of these resins is liquid, having a viscosity at 25 °C lower than about 1000 Pa.s, b) about 15 to about 50 wt.% of at least one multifunctional acrylate compound, c) about 5 to about 30 wt.% of a hydroxyfunctional compound, d) about 1 to about 6 wt.% cationic photoinitiator, e) about 1 to about 6 wt.% free radical photoinitiator. The invention further relates to a process for the manufacturing of 3-dimensional objects, known as rapid prototyping, wherein said photosensitive resin composition is used.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PHOTOSENSITIVE RESIN COMPOSITION FOR RAPID PROTOTYPING AND  
A PROCESS FOR THE MANUFACTURE OF 3-DIMENSIONAL OBJECTS

5

FIELD OF THE INVENTION

The present invention relates to a  
10 photosensitive resin composition for use in rapid  
prototyping, in particular for a method such as  
stereolithography. The resin is made from both a cationic  
curable epoxy resin and a radical curable acrylate  
component. The resin composition has very good properties  
15 such as fast curing, and the cured product has an  
excellent combination of mechanical properties.

BACKGROUND OF THE INVENTION

20 Rapid prototyping with the use of a  
photosensitive resin compositions involves curing of well  
defined areas of resin layers on top of each other to make  
a three-dimensional form that can be used as a prototype,  
or for making a prototype. A prototype, or model, is often  
25 used in order to prepare for making new products.

The resin used in such a process must conform  
with many criteria. The resin composition itself must have  
a certain viscosity. In the curing process, the resin  
composition must cure fast, with a good through cure and a  
30 sufficiently thick layer should be cured, preferably with  
a relatively low light intensity irradiation. The cured  
resin composition should have good green strength  
mechanical properties, good final mechanical properties  
and a relatively low shrink factor on cure.

35 In order to achieve all these properties,  
various resin compositions have been proposed. According  
to US-A-5418112, a suitable resin system consists of an

acrylate oligomer, acrylate functional diluents and a specific photoinitiator system for radical generation. However, radical curable resin systems tend to shrink too much during cure, thereby causing difficulties with precision. Other proposed resin compositions comprise both epoxy functional compounds and acrylate functional compounds; the acrylates are cured using a radical generating photoinitiator, the epoxy using a cation generating photoinitiator. Examples of these resin compositions are e.g. described in EP-A-535828, US-A-5434196 and EP-A-605361. According to EP-A-535828, a suitable resin composition consists of a bisphenol-A based acrylate, an acrylate functional diluent, a cycloaliphatic epoxy functional component and a suitable initiator system that is sensitive to light with a wavelength between 400 and 600 nm. According to US-A-5434196, the cationically curable epoxy resin should be used in combination with a vinyl-ether comprising compound. According to EP-A-605361 a suitable composition consists of an epoxy resin, a cycloaliphatic or aromatic di-acrylate and an hydroxy functional polyether, polyester or polyurethane. The hydroxy functional polymer does react with the epoxy resin. Although the resin compositions have some favorable characteristics, a further improvement in particular with respect to post-cure mechanical properties and accuracy of prototype parts is needed.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a photosensitive resin composition suitable for rapid prototyping which has good mechanical properties.

It is a further object of the invention to provide a resin composition comprising both an epoxy resin and an acrylate functional compound together with cation and radical generating photoinitiators that has a good

stability in that it does not show phase separation on UV-cure.

It is yet another object of the invention to provide such a resin composition with appropriate  
5 photoinitiators which show homogeneous cure with relative low intensity UV-light (on comparison with laser light), good through-cure in at least resin layers of more than 200  $\mu\text{m}$  thickness, which cured resin exhibits good mechanical properties.

10 It is yet another object of the invention to provide a method for manufacturing 3-dimensional objects in which the resin composition according to the present invention is used.

The photosensitive resin composition according  
15 to the invention for use in rapid prototyping comprises  
a. about 30 to about 70 wt.% of at least two epoxy resins; wherein at least one of these resins is solid at room temperature and comprises aromatic groups; and wherein at least one of these resins is liquid,  
20 having a viscosity at 25°C lower than about 1000 Pa.s  
b. about 15 to about 50 wt.% of at least one multifunctional acrylate compound  
c. about 5 to about 30 wt.% of a hydroxyfunctional compound  
25 d. about 1 to about 6 wt.% cationic photoinitiator  
e. about 1 to about 6 wt.% free radical photoinitiator.

Preferably, the amount of the solid epoxy resin(s) is about 10 to about 40 wt.%, more preferably about 15 to about 35 wt.% and the amount of the liquid  
30 resin(s) is about 10 to about 40 wt.%. The liquid epoxy resin, together with the liquid acrylate compounds can be used to adjust the viscosity to a suitable range. In particular the viscosity of the photosensitive resin composition is between about 100 and about 3000 mPa.s,  
35 measured at the application temperature. For laser-cured

rapid-prototyping processes, the viscosity preferably is between about 100 to about 500, whereas the viscosity for processes that uses a photo-mask, the viscosity preferably is between about 1000 to about 3000 mPa.s at the application temperature. The application temperature currently is generally about 30°C to about 32°C.

The resin composition of the present invention exhibits good mechanical properties upon cure. In particular, it is possible to achieve upon full cure a film of about 75  $\mu\text{m}$  thickness having a secant modulus of about 1000 MPa (at 2.5 % elongation) or higher, and an elongation of about 5% or higher, preferably about 8% or higher.

The process of the present invention for the manufacturing of 3-dimensional objects comprises the combination of steps of i. applying actinic radiation to a layer of photosensitive resin in order to cure a pre-determined well-defined area of said resin layer, which area forms a cross-section of said 3-dimensional object; and ii. introducing an uncured layer of resin on top of the cured layer and repeating said curing and introducing steps, wherein the photosensitive resin composition comprises:

- a. about 30 to about 70 wt.% of at least two epoxy resins; wherein at least one of these resins is solid at room temperature and comprises aromatic groups; and wherein at least one of these resins is liquid, having a viscosity at 25°C lower than about 1000 Pa.s
- b. about 15 to about 50 wt.% of at least one multifunctional acrylate compound
- c. about 5 to about 30 wt.% of a hydroxyfunctional compound
- d. about 1 to about 6 wt.% cationic photoinitiator
- e. about 1 to about 6 wt.% free radical photoinitiator.

The process of the present invention is advantageous in case the curing is performed with a laser beam, the laser beam is motion controlled with a computer, with the laser beam focussed on a relatively tiny area of the pre-determined desired to-be-cured area, so as to have the laser beam scan over the to-be-cured area to at least substantially initiate the cure of the photosensitive resin composition. Presently preferred lasers are the helium/cadmium and the argon ion lasers.

Most preferred is a process in which a photomask is used to define the predetermined to-be-cured area and in which said to-be-cured area is exposed to UV-light all at once.

#### DETAILED DESCRIPTION OF THE INVENTION

The first component of the resin composition according to the invention comprises at least two epoxy resins. One of these resins is solid at room temperature and comprises aromatic groups. The other resin is liquid, which means, throughout this specification, having a viscosity at 25°C lower than about 1000 Pa.s.

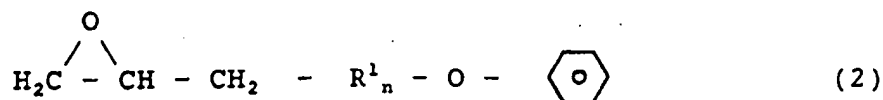
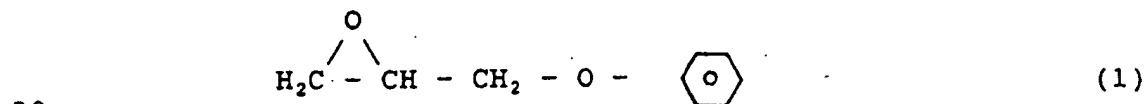
The solid epoxy resin generally is a substantially amorphous polymer, thus, such a resin has a melting range going from the solid to the liquid state.

The melting point of the solid resin preferably is higher than about 30°C. Solid epoxy resins with a melting point higher than about 40°C are particularly preferred. Generally, these epoxy resins have a molecular weight (Mw) higher than about 600. Molecular weight, as used throughout this application, is the calculated molecular weight of the molecule concerned. In case of a polymer structure, it is the calculated molecular weight of the expected structure, based on the starting materials and reaction conditions. The molecular weight can also be determined using conventional techniques.

The liquid epoxy resin has a viscosity at 25°C lower than about 1000 Pa.s, preferably lower than about 100 Pa.s. In general, the molecular weight of such a resin is lower than about 500.

5           The liquid epoxy resin may be aliphatic or aromatic. Preferably, the liquid epoxy resin comprises one or more cycloaliphatic groups, or comprises aromatic groups. Aliphatic epoxy resins give improved cure speed; aromatic epoxy resin result in better storage stability of  
10 the liquid resin. Both types of resins are very suitable as the liquid epoxy resin.

Examples of suitable solid or liquid epoxy resins with aromatic groups are phenol based resins such as epoxidized novolac resins and bis-phenol based resins.  
15 Such resins comprise one or more of the groups according to formula (1) or (2):



25   in which R<sup>1</sup> is an alkoxy group, and n is an integer between 1 and about 12. Preferably, R<sup>1</sup> is an alkoxy with 2, 3 or 4 carbon atoms, in particular ethoxy or propoxy. Preferably, n is smaller than about 6, in particular, n is 1 or 2. Such epoxy resins are made by reaction of  
30 epichlorohydrin with the hydroxyl of the phenol or alkoxyated phenol group.

Particularly preferred are bisphenol resins such as bisphenol-A or bisphenol-F based epoxy resins. These type of resins are commercially available. Both liquid and  
35 solid bis-phenol based epoxy resins exist. Examples of suitable epoxy resins include EPON® resins from Shell such as EPON® 1001, 1002 and 1003. Analogous products exist



e.g. from DOW as DER 661® and higher homologous. Other examples of suitable solids epoxy resins are the epoxy-novolac with about 6 phenol groups and an epoxy equivalent weight of about 200 (ERR 0100 from Union Carbide) and the  
5 polyglycidylether of o-(resol-formaldehyde)Novolac.

Examples of suitable aliphatic liquid epoxy resins are  
bis-4(4-hydroxycyclohexyl)-methane diglycidylether,  
2,2-bis-4(4-hydroxycyclohexyl)-propane diglycidylether,  
10 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate,  
bis-(2,3-epoxycyclopentyl)-ether,  
vinylcyclohexanoxide,  
dicyclopentadiene-dioxyde,  
ethylene-bis-(3,4-epoxycyclohexanecarboxylate),  
15 bis(3,4-epoxycyclohexylmethyl)adipate,  
vinylcyclohexenedioxide,  
3,4-epoxy-6-methylcyclohexyl-3,4-epoxy-6-methyl-  
cyclohexane carboxylate,  
dioctyl-epoxyhexahydrophthalate  
20 and mixtures thereof.

Examples of suitable liquid aromatic epoxy resins are bisphenol-A, optionally with small amounts of higher polymer to prevent crystallization, having an epoxy equivalent weight between 170-200, such as DER® 332, DER  
25 330, DER 331, EPON® 826 and EPON 828. Other suitable liquid epoxy resins are Bisphenol-F (e.g. XD 7818 from DOW), the low molecular weight epoxy novolac resins. Further useful examples of epoxy resins with one aromatic group and one or two epoxy groups are,  
30 p-t-butylphenylglycidylether,  
phenylglycidylether,  
cresylglycidylether, and  
the diglycidylether of resorcinol.

Mixtures of aliphatic and aromatic liquid epoxy  
35 resins can be used as well.

The second component of the resin composition is a multifunctional acrylate or a mixture of such acrylates. This multifunctional acrylate preferably has two or more acrylate or methacrylate functional groups, in particular 5 acrylate groups are preferred because of the improved cure speed obtained therewith. The multifunctional acrylate preferably has less than 8 acrylate groups per molecule. In particular, the number of functional groups is about 2 to about 5. Very useful compositions have been obtained 10 using about 15 to about 35 wt.% of component b.

The resin composition may also comprise up to about 10 wt.% of a monofunctional acrylate functional diluent (apart from component c). Preferred acrylates are aliphatic acrylates. Suitable acrylate functional 15 compounds are acrylate esters of aliphatic (poly)hydroxy compounds. In general, the molecular weight of the acrylate functional compounds is between about 100 and about 2000. Preferably, the molecular weight is lower than about 1000. Suitable acrylate functional compounds 20 include, but are not limited to, trimethylolpropane triacrylate, the triacrylate or methacrylate from hexane-2,4,6 triol, or from glycerol, ethoxylated glycerol, or propoxylated glycerol, 25 hexanediol diacrylate, 1,3-butylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, 30 polyethylene glycol-200 diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate, pentaerythritol tetraacrylate, tripropylene glycol diacrylate, 35 ethoxylated bisphenol-A diacrylate,

- trimethylolpropane diacrylate,  
di-trimethylolpropane tetraacrylate,  
triacrylate of tris(hydroxyethyl) isocyanurate,  
dipentaerythritol hydroxypentaacrylate,  
5 pentaerythritoltriacylate,  
ethoxylated trimethylolpropane triacylate,  
triethylene glycol dimethacrylate,  
ethylene glycol dimethacrylate,  
tetraethylene glycol dimethacrylate,  
10 polyethylene glycol-2000 dimethacrylate,  
1,6-hexanediol dimethacrylate,  
neopentyl glycol dimethacrylate,  
polyethylene glycol-600 dimethacrylate,  
1,3-butylene glycol dimethacrylate,  
15 ethoxylated bisphenol-A dimethacrylate, trimethylolpropane  
trimethacrylate,  
diethylene glycol dimethacrylate,  
1,4-butanediol diacylate,  
diethylene glycol dimethacrylate,  
20 pentaerythritol tetramethacrylate,  
glycerin dimethacrylate,  
trimethylolpropane dimethacrylate,  
pentaerythritol trimethacrylate,  
pentaerythritol dimethacrylate,  
25 pentaerythritol diacylate, and  
the like and mixtures thereof.

- Mono(meth)acrylates such as  
cyclohexyl(meth)acrylate,  
isobornyl(meth)acrylate,  
30 lauryl(meth)acrylate,  
alkoxylated phenolacrylate,  
isooctyl-acrylate,  
2-ethylhexyl-acrylate, and  
tetrahydrofurfuryl(meth)-acrylate are operable, as  
35 reactive diluents.

The third component of the resin composition is an hydroxy functional compound. Excluded from the third component group are epoxy resins comprising hydroxy groups, which are included in the first component group.  
5 Particularly preferred is the use of an amount between about 10 and about 20 wt. %.

The hydroxyl groups react with the epoxy groups, and this hydroxyl functional compound generally is used to make the cured resin more flexible. This compound  
10 preferably is multifunctional and has in a particularly preferred embodiment 2-5 functional groups. The hydroxyl functional compound in general will have a molecular weight higher than about 100 but lower than about 2000. Preferably, the molecular weight is lower than about 1000.

15 Suitable hydroxyl functional compounds are for instance simple multifunctional alcohols, polyether-alcohols, and/or polyesters. Suitable examples of multifunctional alcohols are, trimethylolpropane,  
20 trimethylolethane, pentaeritritol, di-pentaeritritol, glycerol, bisphenol-A,  
25 1,4-hexanediol, 1,4-hexanedimethanol and the like.

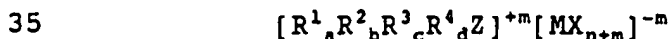
Suitable hydroxyfunctional polyetheralcohols are, for example,  
30 alkoxylated trimethylolpropane, alkoxylated bisphenol-A, in particular the ethoxylated or propoxylated compounds, polyethyleneglycol-200 or -600 and the like.

Suitable polyesters include, hydroxyfunctional polyesters from diacids and diols with optionally small amounts of higher functional acids or alcohols. Suitable diols are those described above. Suitable diacids are, for example, adipic acid, phthalic acid, isophthalic acid, dimer acid, hexahydrophthalic acid, 1,4-cyclohexane dicarboxylic acid and the like. Other suitable ester compounds include caprolactone based oligo- and polyesters such as the trimethylolpropane-triester with caprolactone, Tone®301 and Tone®310. The ester based polyols preferably have a hydroxyl number higher than about 50, in particular higher than about 100. The acid number preferably is lower than about 10, in particular lower than about 5.

Particularly preferred as the hydroxyl functional compound is a hydroxyl functional ester or ether compound with an ethylenically unsaturated group such as a vinylether group, allyl group or, most preferred, a (meth)acrylate group. The use of a compound with both at least one hydroxygroup and at least one - radically- polymerizable group improves the mechanical properties of the cured resin even further. Polycaprolactone based oligo- or polyesters appear to be very suitable compounds for use in the present inventions. Examples of suitable compounds are Tone® M100, polyethylene glycol mono(meth)acrylate, pentaeritritol mono acrylate and the like.

The fourth component is a photosensitive cation generation compound. Cationic photoinitiators are known in the art. Particularly, a group of onium double salts which can generate Lewis acids capable of initiating polymerization by the irradiation are preferred.

Representative examples of the onium double salts include those represented by the general formula:



wherein the cation is an onium;

Z is S, Se, Te, P, As, Sb, Bi, O, halogen (such as I, Br or Cl) or  $N \equiv N$ ;

$R^1 R^2 R^3$  and  $R^4$  may be the same or different from

5 each other and are each an organic group;

a, b, c and d are each an integer of 0 to about

3 with the proviso that the sum total of a, b, c and d is equal to the valance number of Z plus m;

10 M is a central atom of the halide complex and is a metal or metalloid such as B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn or Co;

X is a halogen atom;

m is the net charge of the halide complex ion, and n is

15 the number of halogen atoms in the neutral compound with M.

Preferably m is 1.

Particular examples of the anion  $MX_{n+m}$  of the above general formula include,

20 tetrafluoroborate ( $BF_4^-$ ),  
hexafluorophosphate ( $PF_6^-$ ),  
hexafluoroantimonate ( $SbF_6^-$ ),  
hexafluoroarsenate ( $AsF_6^-$ ), and  
hexachloroantimonate ( $SbCl_6^-$ ).

25 An additional example of a possible salt complex is tetra(pentafluorophenyl)borate ( $B(C_6F_5)_4^-$ ).

Particular preferred examples for Z are S or I (sulphonium or iodonium), the sulphonium being the presently most preferred.

30 Further, anions of the general formula:  $MX_n(OH)^-$  can be used. Other anions which can be used according to the present invention include,  
perchlorate ion ( $ClO_4^-$ ),  
trifluoromethyl sulfite ion ( $CF_3SO_3^-$ ), fluorosulfonate ion  
35 ( $FSO_3^-$ ),

toluenesulfonate anion, and  
trinitrobenzenesulfonate anion.

Particularly preferred as cationic catalyst are  
triaryl sulphonium salts.

- 5           The fifth component of the resin composition is  
a photosensitive radical generating compound or mixture of  
compounds. These photoinitiators are known in the art.  
Suitable photoinitiators include, but are not limited to,  
benzoin,  
10   benzil,  
benzilmethylketal,  
cyclohexylbenzilketal like Irgacure 184,  
benzildimethylketal, and  
the benzoin alkyl ethers, such as benzoin methyl  
15           ether, benzoin ether, benzoin isopropyl ether  
and benzoin isobutyl ether.
- Another class of photoinitiators are the  
dialkoxyacetophenones exemplified by,  
2,2-dimethoxy-2-phenylacetophenone, i.e.  
20           Irgacure®651 (Ciba-Geigy),  
2,2-diethoxy-2-phenylacetophenone,  
benzophenone,  
acetophenone,  
o-methoxybenzophenone,  
25   acenaphthene-quinone,  
methyl ethyl ketone,  
valerophenone,  
hexanophenone,  
alpha-phenyl-butyrophenone,  
30   p-morpholinopropiophenone,  
dibenzosuberone,  
4-morpholinobenzophenone,  
4'-morpholinodeoxybenzoin,  
p-diacetylbenzene,  
35   4-aminobenzophenone,

- 4'-methoxyacetophenone,  
benzaldehyde,  
alpha-tetralone,  
9-acetylphenanthrene,  
5 2-acetylphenanthrene,  
10-thioxanthenone,  
3-acetylphenanthrene,  
3-acetyllindone,  
9-fluorenone,  
10 1-indanone,  
1,3,5-triacetylbenzene,  
thioxanthen-9-one,  
xanthene-9-one,  
7-H-benz[de]-anthracen-7-one,  
15 1-naphtahaldehyde,  
4,4'-bis(dimethylamino)-benzophnone,  
fluorene-9-one,  
1'-acetonaphthone,  
2'-acetonaphthone,  
20 2,3-butanedione,  
acetonaphthene,  
benz[a]anthracene 7,12 diene, etc. The above initiators  
and sensitizing compounds can be used in combination as  
desired.

25 Further suitable sensitizing compounds are for  
example phosphines, such as for instance  
triphenylphosphine and tri-p-tolyl-phosphine.

Each of the cationic cure catalyst and the  
radical cure catalyst can be used in amounts of about 1 to  
30 about 6 wt.%. It is preferred that both catalysts be used  
in such amount that the photoefficiency is substantial  
equal, or that the absorption efficiency is substantially  
equal. In this way, both the radical and cationic cure  
have substantially the same rate of initiation of the



reaction. Preferred amounts are about 1.5 to about 5 wt.% of both initiator compounds.

Although UV-curing is preferred, as the photosensitive compositions are exposed to visible light easily, visible light curable photosensitive compositions have the same advantages. In particular, laser curing can be suitably be performed with visible light-lasers. In that case, the photoinitiator system has to be adapted with the use of suitable sensitizers and/or initiators to give good cure at wavelength of about 400 to about 600 nm.

The composition may further comprise stabilizers in a range of about 0 to about 3% by weight, preferably 0.1 to about 1% by weight. Suitable stabilizers are preferably (hindered) phenols, such as for example 2,6-di-tert-butyl-4-methylphenol and 4-methoxyphenol.

The composition according to the invention may further comprise minor amounts of additional additives such as for example surfactants, dyes, pigments and/or fillers.

The invention is also related to a process for the manufacture of 3-dimensional objects, using the above described resin composition. In particular, the process comprises manufacturing a 3-dimensional object by applying actinic radiation to a layer of photosensitive resin in order to cure a well-defined area of said resin layer. The irradiated area forms a cross section of said object. Next a fresh layer of resin is introduced on top of the cured layer and the curing step is repeated.

A number of ways are known to accomplish the irradiation of a well defined area. One of such methods comprises using a laser and use the focused laser light to cure the resin, such as described in US-A-4575330 and GB-A-2262817. The use of the resin composition according to the present invention in such processes of this type is advantageous because of the resulting very good mechanical

properties, both green strength and as post cured material.

The resin composition according to the invention is preferably used with a rapid prototyping process involving the use of a photomask to build objects. Such a method is, for instance, described in EP-A-322257 and US-A-5519816. In that method, a high power UV lamp is used to flood-expose one layer of a liquid photopolymer at a time through a negative, or mask. The mask is generated electrostatically on a glass plate with a toner powder. A 2 to about 20 second exposure from the lamp will usually be sufficient to solidify a thin surface layer of a photopolymer. The exposed mask is physically wiped clean and electrostatically discharged to prepare it for the next cross-section image. At the same time, the uncured photopolymer, which is still liquid, is blown (air-knifed), vacuumed or washed away. The cavities left by the uncured polymer are filled with hot wax. The wax solidifies to form a support structure for the next layer. Finally, the entire surface is milled with a cutter to make it ready for the next polymer layer. The cycle is repeated, so that the object is built up layer by layer. The resin composition according to the present invention is advantageously used in such a process, not only because of the very good mechanical properties, but also because the resin has the capability of achieving good through cure (no phase-separation on cure), with sharp cured-uncured boundaries, very little photomask contamination, and high precision at thin walled parts.

The invention will be further elucidated with the following examples, which are provided for the purpose of illustrating the practice of the invention, and which are not intended to limit the invention nor the scope of the claims.

Examples I-IV

The components as listed in table 1, except for the initiators, were mixed (the amounts in wt.%) carefully at 70°C for about 3 hours until the mixture was homogeneous. The mixture was then cooled and the initiators were added and mixed in.

Table 1

Component	Description	I	II	III	IV
EPON 1001F	Solid Bisphenol-A epoxy resin	25	27.5	25	17.5
EPON 828	Liquid Bisphenol-A epoxy resin	23	10	25	40
SR 454	ethoxylated trimethylolpropane triacrylate	28	47.5	20	28
Tone 100	caprolactoneacrylate	20		25	10
Tone 301	caprolactonetriol		10		
UVI 6974	cationic initiator	2	2.5	2.5	2
Irgacure 184	Free-radical initiator	2	2.5	2.5	2.5

The viscosity of each of the resin mixtures was measured at 32°C, and reported in Table 2. The cure depth and rosette for each resin mixture was measured using a 10 sec. exposure with a total energy of .09 Joules/cm<sup>2</sup> from a Fusion D bulb. The rosette value defines the level of optical density just below that which will cause gel formation. Preferably, for the type of rapid prototyping processes that use a photomask, the rosette value is

between about 40% and about 60%, at the exposure energy level employed.

Furthermore, a 75  $\mu\text{m}$  thick film was drawn on a glass film, and cured by exposure to 2 J/cm<sup>2</sup> of UV light.

5 Next, the film was post-cured for 1 hr. at 88°C.

From the cured film the mechanical properties were measured. The results are shown in Table 2.

Table 2

10	Characteristic	I	II	III	IV
	viscosity (mPa.s)	1735	2081	1730	1440
	cure depth ( $\mu\text{m}$ )	309	493	267	333
	Rosette value (%)	35	50	40	40
	Tensile strength (MPa)	54	54	48	65
15	Elongation (%)	6	5	16	3
	Modulus (MPa) <sup>1)</sup>	1568	1668	1550	2230
	Tg (°C)			63	96

<sup>1)</sup> Secant modulus, measured at 2,5% elongation.

20

Further, if cured through a photomask, the resins compositions exhibited a substantially homogeneous cure, whereas, by contrast, a composition with a  
25 cycloaliphatic epoxy resin suffered from an uncured resin layer at the bottom of a cured film.

Examples V-IX

Further, several resin mixtures were prepared and tested in an analogous way to Examples I-IV. The components are shown in table 3, the results in table 4.

5

Table 3

Component	Description	V	VI	VII	VIII	IX
EPON 1001F	solid bisphenol-A epoxy resin	32.5	30.5	23.7	27.0	30.3
UVR 6105 <sup>(1)</sup>	liquid cycloaliphatic epoxy resin	17.0	19.0			19.0
10 UVR 6128 <sup>(2)</sup>	liquid cycloaliphatic epoxy resin			14.2	22.5	
Photomer 3016	epoxy acrylate			11.4		
Tone M100	caprolactone acrylate	22.5	20.0	14.2	13.0	25.0
SR 454 <sup>(3)</sup>	tri-acrylate	22.5		31.3	32.0	20.0
15 SR 499 <sup>(4)</sup>	tri-acrylate		25.0			
UVI 6974	cationic photoinitiator	2.5	2.5	2.4	2.5	2.5
Irgacure 184	free radical photoinitiator	3.0	3.0	2.8	3.0	3.2

- 20 <sup>(1)</sup> 3,4-epoxycyclohexyl-3,4-epoxycyclohexanecarboxylate  
<sup>(2)</sup> bis(-3,4-epoxycyclohexyl)adipate  
<sup>(3)</sup> SR454 ethoxylated trimethylolpropane-triacrylate  
(3 Eth.)

(4) SR 499 ethoxylated trimethylolpropane triacrylate  
(6 Eth.)

Table 4

5	Characteristic	V	VI	VII	VIII	IX
	viscosity (mPa.s)	1825	1620	1670	1378	1531
	cure depth ( $\mu\text{m}$ )	394	604	270	350	340
	rosette value (%)	50	55	50	58	50
	tensile strength (MPa)	52	43	53	54	55
10	elongation (%)	7	29	7	8	8
	secant modulus	1569	1261	1100	1170	1290

C L A I M S

1.   Photosensitive resin composition for rapid  
     prototyping comprising:
  - 5       a.   about 30 to about 70 wt.% of at least two epoxy  
          resins, wherein at least one of these resins is  
          solid at room temperature and comprises aromatic  
          groups, and wherein at least one of these resins  
10       is liquid, having a viscosity at 25°C lower than  
          about 1000 Pa.s
  - b.   about 15 to about 50 wt.% of at least one  
          multifunctional acrylate compound;
  - c.   about 5 to about 30 wt.% of a hydroxyfunctional  
          compound;
  - 15       d.   about 1 to about 6 wt.% of a cationic  
          photoinitiator; and
  - e.   about 1 to about 6 wt.% of a free radical  
          photoinitiator.
2.   Resin composition according to claim 1, wherein the  
20       composition comprises:
  - a.1. about 15 to about 35 wt.% of the at least one  
          solid epoxy resin, and
  - a.2. about 10 to about 40 wt.% of the at least one  
          liquid epoxy resin.
- 25   3.   Resin composition according to any one of claims 1-2,  
      wherein the liquid epoxy resin comprises a  
      cycloaliphatic group.
4.   Resin composition according to any one of claims 1-2,  
      wherein the liquid epoxy resin comprises an aromatic  
30       group.
5.   Resin composition according to any one of claims 1-4,  
      wherein the at least one multifunctional acrylate has  
      about 2 to about 5 functional groups.

6. Resin composition according to any one of claims 1-5, wherein the hydroxyl functional compound has about 2 to about 5 functional groups.
7. Resin composition according to any one of claims 1-6, wherein the hydroxyl functional compound comprises at least one hydroxyl group and at least one ethylenic unsaturated group.
8. Resin composition according to claim 7, wherein the ethylenic unsaturation is methacrylate or acrylate.
9. Resin composition according to any one of claims 1-8, wherein the cationic photoinitiator is a triarylsulphonium salt.
10. Resin composition according to any one of claims 19, wherein the composition has a viscosity between about 100 to about 3000 mPa.s at the application temperature.
11. Resin composition according to any one of claims 1-10, wherein the composition when suitably cured in the form of a film of about 75  $\mu\text{m}$  thickness has a secant modulus at 2.5% elongation of more than about 1000 MPa and an elongation higher than about 5%.
12. Process for manufacturing 3-dimensional objects comprising the combination of steps of:
  - i. applying actinic radiation to a layer of photosensitive resin composition according to any one of claims 1-11; in order to cure a pre-determined area of said resin layer, which area forms a cross-section of said 3-dimensional object; and
  - ii. introducing an uncured layer of resin on top of said cured layer and repeating said curing and introducing steps.
13. Process according to claim 12, wherein curing is performed with a laser beam, said laser beam being motion controlled with a computer so as to have said



laser beam scanned over the pre-determined area to-be-cured in order to at least substantially initiate the cure of said photosensitive resin composition.

- 5 14. Process according to claim 13, wherein a photomask is used to define the pre-determined area to-be-cured, and wherein the pre-determined area to-be-cured is substantially all-at-once exposed to UV-light.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00261

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G03F7/027

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 476 748 A (STEINMANN BETTINA ET AL) 19 December 1995 see the whole document	1
A	& EP 0 605 361 A (CIBA GEIGY AG) 6 July 1994 cited in the application	
A	EP 0 535 828 A (ICI PLC) 7 April 1993 cited in the application see the whole document	1
A	US 5 434 196 A (OHKAWA KAZUO ET AL) 18 July 1995 cited in the application see the whole document	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

18 July 1997

Date of mailing of the international search report

11.08.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Heywood, C

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL 97/00261

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 657 779 A (GASKE JOSEPH E) 14 April 1987 see the whole document -----</p>	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00261

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5476748 A	19-12-95	AT 151085 T	15-04-97
		AU 658780 B	27-04-95
		AU 5252493 A	30-06-94
		CA 2111718 A	22-06-94
		DE 59306034 D	07-05-97
		EP 0605361 A	06-07-94
		ES 2100513 T	16-06-97
		JP 6228413 A	16-08-94
EP 0535828 A	07-04-93	JP 5086149 A	06-04-93
US 5434196 A	18-07-95	JP 1213304 A	28-08-89
		JP 8026121 B	13-03-96
		JP 2028261 A	30-01-90
		JP 2590215 B	12-03-97
		JP 2080422 A	20-03-90
		JP 2080423 A	20-03-90
		JP 2538652 B	25-09-96
		US 5525645 A	11-06-96
		EP 0360869 A	04-04-90
		WO 8907620 A	24-08-89
US 4657779 A	14-04-87	CA 1289688 A	24-09-91
		WO 8705540 A	24-09-87